Some Considerations about the Durability of Historic Mortars

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Abstract

The current manuscript discusses the durability of historical mortars. The majority of the descriptions about those mortars are mainly related to the Roman period and refer the mixture of calcium hydroxide and pozzolans (volcanic ashes and calcined clays) as the right recipe to get strong and durable binders. Those descriptions lack explanations about the reaction mechanisms that could explain the durability of those mortars, not can they explain the presence of analcime zeolites that several researchers found in historical mortars. The present manuscript discusses the durability of historical mortars trough the alkali-activation theory, according to which geopolymeric compounds and calcium silicate hydrates are responsible for the durability of historical mortars.

Keywords: alkali-activated; binders; durability; pozzolans

1. INTRODUTION

The durability of historic mortars is an issue some how related to the low durability of portland cement, the binder most used by the construction industry in the last 100 years. The truth is that ordinary Portland Cement (OPC) concrete structures deterioration is a very common phenomenon. OPC structures which have been build a few decades ago are still facing disintegration problems points out the durability handicaps of OPC binders. In fact the number of premature cases of OPC structures disintegration is overwhelming. Mehta [1] mentioned a case of pile foundations disintegrated just after 12 years and also the case of a tunnel in Dubai, which have been concluded in 1975 and needed to be completely repaired in 1986. Gjorv [2] mentioned a study about Norway OPC bridges which indicate that 25 % of the ones build after 1970 presented corrosion problems. Another author mentioned that 40% of the 600.000 bridges in the U.S. were affected by corrosion problems being estimated in 50 billion dollars the cost of the repairing operations [3]. Beyond the durability problems originated by imperfect concrete placement and curing operations, the real issue about OPC durability is related to the intrinsic properties of that material. Presents a higher permeability that allows water and other aggressive elements to enter concrete, leading to carbonation and corrosion problems. It also presents a higher amount of calcium hydroxide, which reacts with acids generating soluble compounds.

By the other side, literature often reveals countless cases of historical constructions that survived trough out ancient times showing a remarkable durability. Malinowsky [4], report the use of portland cement to repair ancient constructions, having noticed that material was deteriorated just after 10 years, making clear is low performance when compared to historical mortars durability. Several authors Shi & Day [5], Baronio & Binda [6] and Sabir et al. [7], who investigate about pozolanic reactivity report the unsual durability of mortars made by pozzolans and lime, however none of them explains why is that so. More recently Varela & Vieira [8] explain that the durability of Roman mortars were due to the combination of pozzolans and lime. Unfortunately they

lack to present a reaction mechanism for it. Alvarez et al. [9], reports the work of *Vitruvius* which describes several Roman mortars like *Opus cementicium, Coccio pisto* or *Opus Signinum*, still those authors lack to give some explanation about the durability of those mortars.
Therefore the purpose of that manuscript is to present a less classic explanation about historical mortars durability.

2. SOME RELEVANT HISTORICAL MORTARS INVESTIGATIONS

Roy [10] suggests that calcined clays mix with slaked lime (calcium hydroxide) were the first hydraulic binder made by men. The use of lime based binder mixtures dates back to the 6th millennium BC. A terrazzo floor excavated in Estearn Turkey laid with a lime mortar has been dated between 12000 and 5000 BC. A lime mortar used for flooring fishmen´s huts excavated at Serbia-Montenegro has been dated at about 5600 BC [11]. Malinowsky [12] reports ancient constructions from 7000 B.C in the Galilei area (Israel) using this type of binder. The Roman mortars used for the Hadrian´s wall in Britain were made of crushed ceramic material mixed with lime binder [13]. Hazra & Krishnaswamy [14] mentioned that those mortars were use by the Roman Civilization to build houses, bridges and aqueducts. Crushed ceramics seem also to be preferred from early Hellenistic to early Byzantine times in mortars related to water-bearing constructions and to protect the inside of walls from moisture, typically in baths, canals and aqueducts [15,16]. To Lea [17] and Bogue [18] several of the monuments that survived to the twenty first century like the triumphal arches of the Emperors Claudius and Trajan in Ostia or the bridges of Fabricus, Aemilius, Elius e Milvius shows the durability of historical mortars.
Altough historical mortars made with pozzolanic materials (volcanic-sand *harena fossicia*, grounded clay brick or tiles-*testa,* calcined kaolonitic clay-*carbunculus)* led to an increase strength due to the formation of CSH compounds, some authors do not believe that is the main reason beyond historical mortars durability. For instance because those binders have low Ca/Si molar ratio, lower than traditional ratios for OPC based binders. But mainly because historical binders present an unsual high amount of alkali earth metals. In 1959 Glukhovsky [19], report some investigations about the binders used in ancient Roman and Egyptian constructions. Having concluded they were composed of aluminosilicate calcium hydrates similar to the ones of portland cement and also of crystalline phases of analcime, a natural rock that would explain the durability of those binders. In the 70´s other authors also reported the existence of almost 40% of analcite zeolites in the composition of mortars found in Jericho in the valley of the Jordan river and also in Tel-Ramad Siria, as old as 7000 B.C. [20-22]. Other researchers had analyze Roman mortars having also found the presence of analcime [23,24]. Campbell & Folk [25] showed that the durability of ancient binders was due to its high level of amorphous zeolitic compounds. Also Granizo [26] thinks that the presence of zeolitic compounds in several ancient binders suggests they are the final stable phase of a log term conversion of the primary phases to zeolite-like materials. Also the fact that alkali-activated binders could be considered pozzolanic cements is also raised by some authors [27,28].

3. ABOUT ALKALI-ACTIVATED BINDERS

Table 1 presents a historical background about important events in the field of alkali-activated binders [29]. The development of alkali-activated binders had a major contribution in the 40´s with the work of Purdon [30]. That author have use blast furnace slag (BFS) activated with sodium hydroxide. According to him the process was developed in two steps. During the first one, liberation of silica aluminium and calcium hydroxide took place. After that the formation of silica and alumina hydrates would

happen as well as the regeneration of the alkali solution. His results led him to conclude that alkali hydroxides acted as catalysts, having proved that statement by leaching alkali hydroxides in the same amount as presented in the original mixture. Although one may consider that the work of Feret [31] was a relevant one in this field of experty. That work is more about revision of the use of BFS mixed with Portland cement than about the alkali-activated binders. Based in his investigations about ancient constructions Glukhovsky developed a new type of binders that he names as "*soil-cement*", the word soil because it seemed like a ground rock and the word cement due to its cementitious capacity. The "*soil-cement*" was obtained from ground aluminosilicate mixed with rich alkalis industrial wastes. Investigations in the field of alkali activation had an exponential increment after the research results of the French author Joseph Davidovits [32] which developed and patented binders obtained from the alkali-activation of metakaolin, having named it after the term geopolymer in 1978.

Table 1 – Bibliographic history of some important events about alkali-activated binders [29].

Author	Year	Significance
Feret	1939	Slags used for cement
Purdon	1940	Alkali-slag combinations
Glukhovsky	1959	Theoretical basis ans development of alkaline cements
Glukhovsky	1965	First called "alkaline cements"
Davidovits	1979	" Geopolimer" term
Malinowski	1979	Ancient aqueducts characterized
Forss	1983	F-cement (slag-alkali-superplasticizer)
Langton e Roy	1984	Ancient building materials characterized
Davidovits e Sawyer	1985	Patent of " Pyrament " cement
Krivenko	1986	D.Sc Thesis, R_2O – RO - SiO_2 - H_2O
Malolepsy e Petri	1986	Activation of synthectic melilite slags
Malek. et al.	1986	Slag cement-low level radioactive wastes forms
Davidovits	1987	Ancient and modern concretes compared
Deja and Malolepsy	1989	Resistance to chlorides shwon
Kaushal et al.	1989	Adiabatic cured nuclear wastes forms from alkaline mixtures
Roy and Langton	1989	Ancient concretes analogs
Majundar et al.	1989	$C_{12}A_7$ – slag activation
Talling and Brandstetr	1989	Alkali-activated slag
Wu et al.	1990	Activation of slag cement
Roy et al.	1991	Rapid setting alkali-activated cements
Roy and Silsbee	1992	Alkali-activated cements: an overview
Palomo and Glasser	1992	CBC with metakaolin
Roy and Malek	1993	Slag cement
Glukhovsky	1994	Ancient, modern and future concretes
Krivenko	1994	Alkaline cements
Wang and Scrivener	1995	Slag and alkali-activated microstructure

According to Davidovits, geopolymers are polymers because they transform, polymerize and harden at low temperature. But also they are Geo-polymers, because they are inorganic, hard and stable at high temperature and also non inflammable.
According to that author, the new binder is generated by an adjustment of the process used by the roman and the Egyptians. Davidovits even suggests that the pyramids have not been made with natural stone but instead were made of man made binders. Based on chemical and mineralogical studies he stated that the pyramid blocks were made of a mixture, with limestone sand, calcium hydroxide, sodium carbonate and water. According to his investigations, pyramid blocks were not made of calcium fossilized layers as it happens in natural stones, but oriented in a random manner as in an artificial binder. XRD diffraction patterns of pyramid specimens indicate that ($CaCO_3$) is the major crystalline phase, however an amorphous material composed of

aluminosilicates and a zeolite like material ($Na_2O.\ Al_2O_3.4SiO_2.\ 2H_2O$) were also found [33]. For the chemical designation of the geopolymer Davidovits suggests the name (poliysialates), in which Sialate is an abbreviation for aluminosilicate oxide. The sialate network is composed of tetrahedral anions $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ sharing the oxygen, needing positive ions such as (Na^+, K^+, Li^+, Ca^{++}, Na^+, Ba^{++}, NH_4^+, H_3O^+) to compensate the electric charge of Al^{3+} in tetrahedral coordination (after dehydroxilation the aluminium changes from coordination 6 (octahedral) to coordination 4 (tetrahedral).

The Polysialate have the follow empiric formulae:

$$M_n\{-(SiO_2)_z-AlO_2\}_n,\ w\ H_2O$$

where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium, generating different types of Poly(sialates) (Fig. 1).

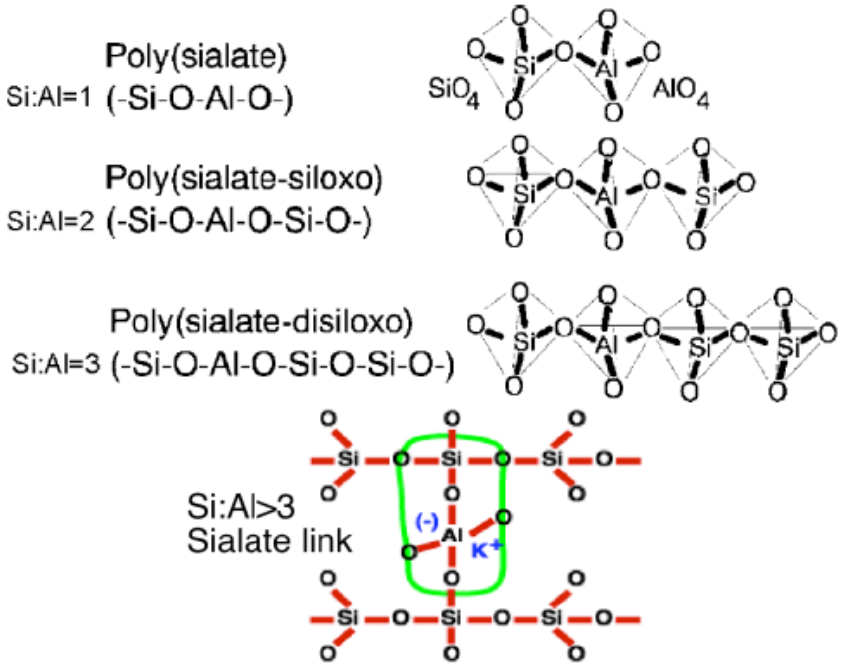

Fig. 1 – Types of Poly(sialates) [34]

Although these new binders have been named has alkaline cements or alkali-activated cements, this name is hardly peaceful. Because of the founding's and designations introduced by Davidovits. Over the last few years that author had argue that the designation alkali-activated binders is confuse and may wrongly induce civil engineers. Let them think it could generate alkali-silica reactions. Suggesting other names such as Geopolymer cement, Geopolymeric cimentitious compounds, Geocements or Poly(sialates). However if Davidovits has some cause about the ambiguity of the name alkali-activated cement, for the other hand its not easy to accept the reason related to the fact that it may mislead engineers about the alkali-silica reaction. Besides its not granted that all alkali-activated binders are really geopolymers. So one believes that the general rule is to use the name alkali-activated binders and the name geopolymer should only be used when we are really in the presence of a geopolymer, a zeolite with amorphous to semi-crystalline characteristics. The exact reaction mechanism which explains the setting and harden of alkali-activated binders is not yet quite understood, although one thinks it depends on the prime material as well as on the alkaline

activator. According to Glukhovsky [28] the mechanism of alkali-activation is composed of conjoined reactions of destruction-condensation, that include the destruction of the prime material into low stable structural units, their interaction with coagulation structures and the creation of condensation structures. The first steps consists of a breakdown of the covalent bonds Si-O-Si e Al-O-Si, which happens when the pH of the alkaline solution raises, so those groups are transformed in a colloid phase. Then it follows a accumulation of the destroyed products, that interacts among them to form a coagulated structure, leading in a third phase to the generation of a condensed structure. Other authors believe that two different models of alkali-activation could be established [36]:

The first one is the case of the activation of BFS (Si+Ca) with a mild alkaline, having CSH as the main reaction products. In the second model of alkali activation (Si+Al), the general example is the alkali-activation of metakaolin with medium to high alkaline solutions, the final product is characterized by a polymeric model and high mechanical strength. The former model applies to aluminosilicate materials and has similarities with the zeolite formation process patented by Davidovits. Although Davidovits investigations used aluminosilicate materials calcium free. The fact is that Pyrament cement is composed by 80% of portland cement (allegedly due to its low cost) and also by 20% of geopolymeric materials activated by potassium carbonate having citric acid as a retarder [37]. Also the patented geopolymeric cements PZ-Geopoly® and Geopolycem® have 11% of CaO in their composition [38] confirming the importance of calcium in alkali-activated binders.

Recent investigations by Yip & Deventer [39] show that a certain amount of calcium oxide seems to be responsible for increase strength in geopolymer mixtures due to the formation of Ca-Al-Si amorphous structures. Those authors reported the coexistence of geopolymeric gel and CSH (Fig. 2) being that the former phase acts as microaggregates and suggested that the formation of those two phases would explain the durability of ancient binders.

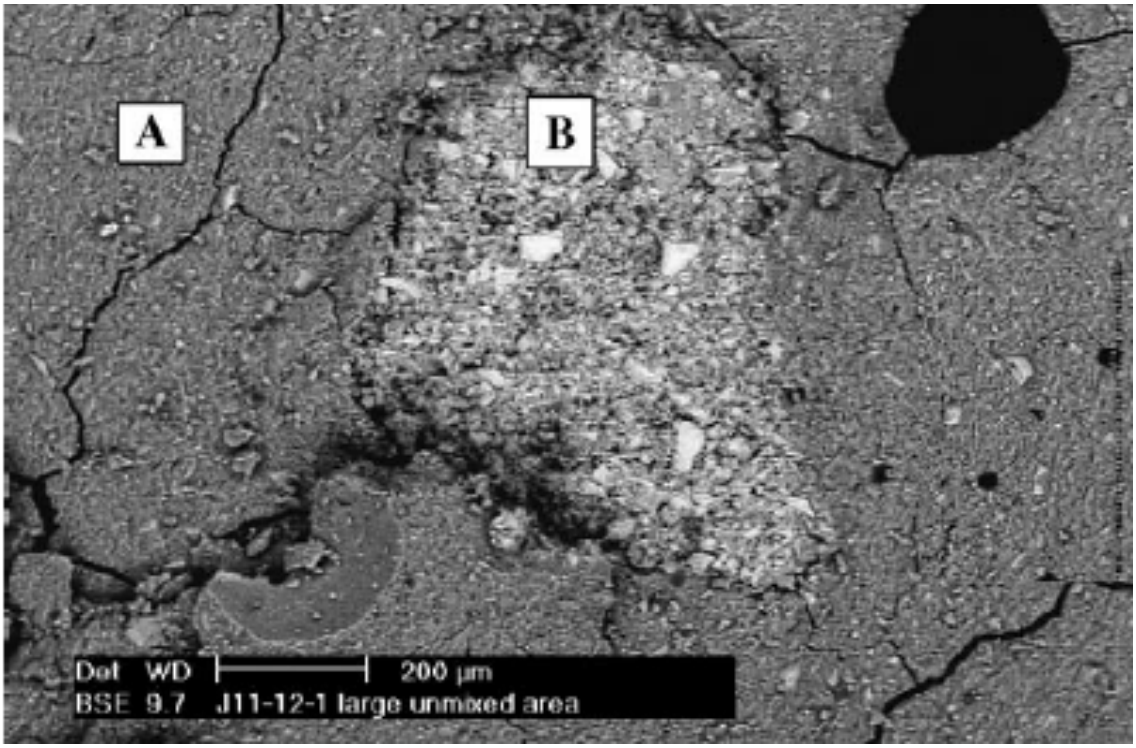

Fig. 2 – Formation of geopolimeric gel (A) and CSH gel (B) [39]

Geopolymeric binders show high compressive and flexural strength after just one day curing and they can easily achieved a compressive strength of 100MPa. As for acid resistance geopolymeric binders perform a lot better than OPC binders. Davidovits [30] report the case of several specimens immersed during 4 weeks in sulphuric acid. After that period geopolymeric specimens show a 7% mass loss but OPC specimens had almost 95% mass loss. That performance which shows the unusual durability of geopolymeric binders can give us some insights to better understand historical mortars durability.

4. CONCLUSIONS

Historical mortars capabilities to endure from ancient times to the twenty first century are a remarkable sign of their durability. The explanation for that behaviour cannot rely solely upon the mixture of powdered ceramic material mixed with lime binder, because that explanation forgets the role played by the high amount of zeolitic compounds found in those mortars. According to the alkaline activation theory historical mortars are the result of a new type of binder in which geopolymeric gel and CSH coexist and act as one.

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